

# The Selective Pathway to Higher Oxygenates from CO, H<sub>2</sub>, Olefins, and Chlorocarbons

Raja Krishnamurthy, Steven S. C. Chuang\*, Mark A. Brundage and Michael W. Balakos  
Department of Chemical Engineering,  
The University of Akron,  
Akron, OH 44325-3906, U.S.A.

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The synthesis of higher oxygenates from CO hydrogenation, ethylene addition and methylene chloride addition to syngas has been studied over Rh/SiO<sub>2</sub> catalyst. The insertion of linear CO into the adsorbed alkyl intermediates is the key step in the formation of higher oxygenates. Pulse transient technique incorporated with *in situ* infrared (IR) technique reveals that hydrogenation of acyl species is the rate limiting step for propionaldehyde formation. Increasing total pressure increases the residence time of alkyl intermediates for CO insertion.

## INTRODUCTION

The synthesis of higher oxygenates from CO and related reactions involves a number of elementary steps: (i) the formation of alkyl intermediates, (ii) the insertion of linear CO into the adsorbed alkyl intermediates to form acyl intermediates, and (iii) hydrogenation of the acyl intermediates (1-3). Figure 1 shows the possible reaction pathway for the formation of alkyl intermediates. Alkyl intermediates can be formed from (i) CO dissociation and hydrogenation in the CO and H<sub>2</sub> reaction (4,5), (ii) partial hydrogenation of an olefin, such as ethylene, in the CO/H<sub>2</sub>/Olefin reaction (6), and (iii) dehalogenation of chloromethanes in the CO/H<sub>2</sub>/CH<sub>3</sub>Cl<sub>4-x</sub> reaction (7).

The selectivity towards oxygenates depends on the ratio of hydrogenation rate to the CO insertion rate. Design of a selective catalyst for C<sub>2+</sub> oxygenate synthesis requires an understanding of the reactivity of alkyl group towards hydrogenation and CO insertion reaction steps. This paper reports the use of *in situ* IR and dynamic approach to study the nature of active sites and elementary steps involved in the higher oxygenate synthesis from CO/H<sub>2</sub> and CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reactions (8).

## EXPERIMENTAL

### Catalyst Preparation and Characterization

4 wt% Rh/SiO<sub>2</sub> catalyst was prepared from RhCl<sub>3</sub>·3H<sub>2</sub>O solution by incipient wetness impregnation method. After impregnation the catalyst was dried overnight in air at 300 K and then reduced in flowing hydrogen at 673 K for 16 hr. The exposed metal atoms was determined to be 244 μmol/g by H<sub>2</sub> pulse chemisorption at 303 K assuming an adsorption stoichiometry of H<sub>ads</sub>/Rh = 1.

### Reaction Studies

CO hydrogenation, ethylene addition, and methylene chloride addition were carried out in a differential reactor system. Space velocities of 11,000 h<sup>-1</sup> were used to keep the CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. Methylene chloride was added to the reactant gas mixture by bubbling hydrogen through a saturator filled with CH<sub>2</sub>Cl<sub>2</sub> at 273 K. The product distribution was determined using a HP-5890A gas chromatograph (GC) with a 6 ft. Porapak PS column in series with a 6 ft. Porapak QS column.

### Steady State Isotopic Pulse Transient Studies

The prepared catalyst was pressed into a self-supporting disk and placed in an IR reactor cell capable of operating up to 723 K and 6.0 MPa. The catalyst was further reduced *in situ* at 673 K for 1 hr before each experiment. Steady-state flow of CO/H<sub>2</sub> was admitted to the reactor. A 6-port GC

\* Author to whom correspondence should be addressed

sampling valve was used to inject 10 cm<sup>3</sup> of isotopic species into the steady-state CO flow which created a positive <sup>13</sup>CO pulse and a negative <sup>12</sup>CO pulse with symmetry as shown in Fig 2 (a). The symmetric response indicates that <sup>12</sup>CO was replaced by <sup>13</sup>CO at a 1 to 1 ratio and total CO (<sup>12</sup>CO and <sup>13</sup>CO) flow was maintained at steady-state. It should be noted that proper balancing of <sup>13</sup>CO pressure in the sampling loop and the <sup>12</sup>CO flow line is essential for maintaining steady-state flow conditions. The reactant <sup>12</sup>CO gas contains 2% Ar which is used to determine the effect of gas holdup in the reactor and the transportation lines on the transient response of gaseous products (Fig 2). Main components in the effluent of the IR cell were monitored by a mass spectrometer (MS). The change in the IR spectra of adsorbed species with time during the <sup>13</sup>CO pulse was monitored by an FTIR spectrometer. The composition of the product gas was determined by the gas chromatograph.

## RESULTS AND DISCUSSION

CO hydrogenation over Rh/SiO<sub>2</sub> produced methane as major product and C<sub>2</sub>-C<sub>5</sub> hydrocarbons as minor products in the temperature range of 473 - 573 K and 0.1 MPa. No oxygenated product was produced at 0.1 MPa. Increasing reaction pressure to 0.4 MPa led to the formation of acetaldehyde. The higher oxygenate selectivity increases with reaction pressure (8). The effect of reaction pressure on oxygenate selectivity was studied by steady-state isotopic pulse transient. Residence time of reactants in the reactor cell for the 0.4 MPa runs was kept the same as for the 0.1 MPa runs by increasing the total flow rate from 60 cm<sup>3</sup>/min to 240 cm<sup>3</sup>/min.

The responses of <sup>13</sup>CH<sub>4</sub> and CH<sub>3</sub><sup>13</sup>CHO to <sup>13</sup>CO pulse at 0.1 MPa and 0.4 MPa are shown in Figure 2 (a) and (b). The residence time,  $\tau$ , of intermediate to products is determined by the following equation (9)

$$\tau = \int_0^{\infty} tE(t)dt - \tau_{av}$$

$\tau$  for methane was determined to be 0.14 and 0.54 min for CO hydrogenation at 0.1 MPa and 0.4 MPa, respectively. Increasing reaction pressure increased the  $\tau$  for CH<sub>4</sub> suggesting that CH<sub>x</sub> for hydrogenation stays on the surface longer at high pressure than at low pressure.  $\tau$  for CH<sub>3</sub>CHO is smaller than that for CH<sub>4</sub> at 0.4 MPa. Formation of acetaldehyde at high reaction pressure can be explained by the increase in residence time of CH<sub>x</sub> intermediates at high CO/H<sub>2</sub> pressure allowing CO insertion to occur.

An alternate approach to increase C<sub>2</sub> oxygenate selectivity is to increase the surface concentration of alkyl intermediates. Addition of CH<sub>2</sub>Cl<sub>2</sub> to CO/H<sub>2</sub> has been found to result in the formation of acetaldehyde on Rh/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> at 0.1 MPa (10,11). Increasing methyl concentration accelerates the rate of CO insertion resulting in the formation of C<sub>2</sub> oxygenates. Such a process even occurs on Ni/SiO<sub>2</sub>, which exhibits little CO insertion activity during CO hydrogenation. Increasing ethyl intermediate concentration by the addition of ethylene to CO/H<sub>2</sub> over Ni/SiO<sub>2</sub> can also lead to the formation of propionaldehyde, the product of CO insertion (12). The mechanism of the formation of propionaldehyde from CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> was further studied by isotopic pulse transient technique over Rh/SiO<sub>2</sub>.

Figure 3 shows a response of a 10 cm<sup>3</sup> pulse of <sup>13</sup>CO into <sup>12</sup>CO/Ar flow at 0.1 MPa and 503 K during the CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction. The figure shows the transient response for Ar, <sup>12</sup>CO, <sup>13</sup>CO, and C<sub>2</sub>H<sub>5</sub><sup>13</sup>CHO. The symmetrical nature of the <sup>12</sup>CO and <sup>13</sup>CO response indicates that the species displaced each other and the total concentration of CO, isotopic and non-isotopic, remained the same during the pulse. Steady-state reaction conditions were maintained during the isotopic pulse transient study. The lag time between the argon and the CO response is due to the interaction of the gas phase CO with the adsorbed CO, i.e., adsorption and desorption effects. The time delay in the <sup>13</sup>C propionaldehyde response corresponds to the residence time of the <sup>13</sup>C surface intermediates leading to the formation of propionaldehyde. Modeling results reveal that the hydrogenation of the acyl intermediate is the rate-determining step for the formation of propionaldehyde (13).

## CONCLUSION

The higher oxygenate formation on Rh catalysts involve a key CO insertion step. The linearly adsorbed CO is inserted into the adsorbed hydrocarbon intermediate formed from reaction of chlorinated hydrocarbons and ethylene and CO hydrogenation. Hydrogenation of the acyl intermediate is the rate-determining step for the formation of propionaldehyde from CO/H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>. The higher oxygenates selectivity can be increased by increasing reaction pressure during CO hydrogenation, and addition of CH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>.

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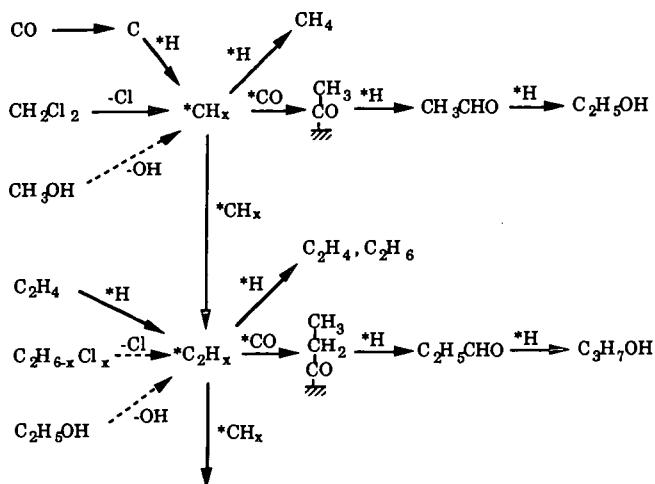


Figure 1. Proposed reaction pathway for syngas related reactions.

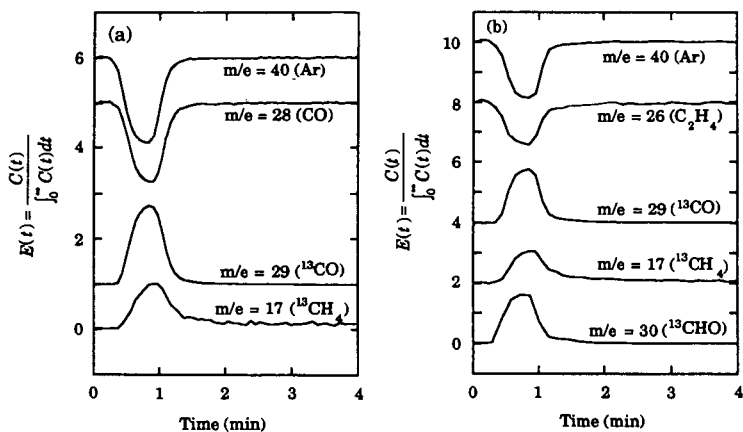


Figure 2. MS response to  $^{13}\text{CO}$  pulse in  $\text{CO}/\text{H}_2$  on  $\text{Rh}(\text{Cl})/\text{SiO}_2$  at 543 K and (a) 0.1 MPa and (b) 0.4 MPa.

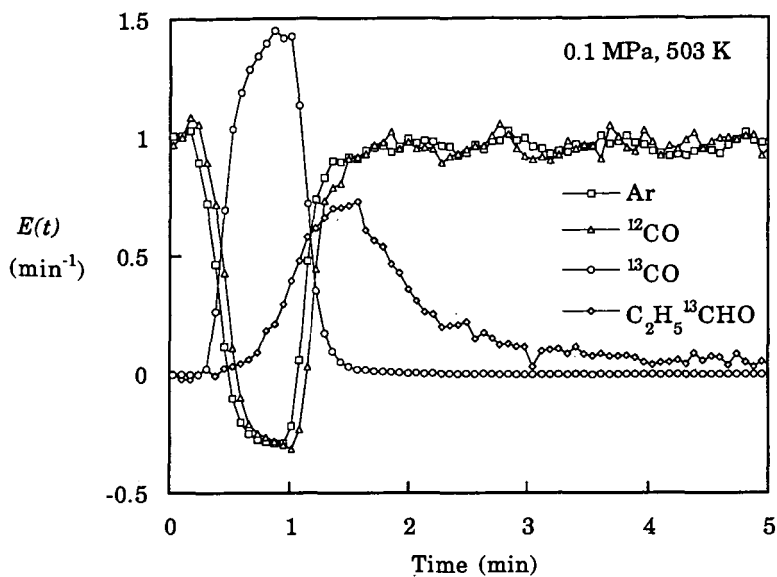


Figure 3. Transient response of Ar,  $^{13}\text{CO}$ , and  $\text{C}_2\text{H}_5\text{ }^{13}\text{CHO}$  to a pulse of  $^{13}\text{CO}$  in  $^{12}\text{CO}$  flow during ethylene hydroformylation on 4 wt% Rh/SiO<sub>2</sub> at 503 K and 0.1 MPa